

# Suitability of Extraction Systems with Macrocyclic Ligands for the Study of Rutherfordium

## 1. Zr and Hf Extraction with Dicyclohexano-18-crown-6

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Recently, the fast automated liquid-liquid extraction system SISAK was successfully used to study the chemical behavior of element 104, rutherfordium [1]. This was made possible by coupling the SISAK system to the Berkeley Gas-filled Separator (BGS). The BGS was used to achieve a physical pre-separation of the desired species from the beam and unwanted reaction products.

When using a physical pre-separator, selectivity between the members of the same group of the periodic table can now be favored over efficient separation from elements belonging to other groups when designing extraction systems for future experiments [2]. As a result the usefulness of previously used extraction systems should be reevaluated and other classes of extraction systems can now be considered as well.

Based on the first successful experiments with pre-separated rutherfordium isotopes, it was decided to start a search for different highly selective extraction systems that could be used to study the chemistry of rutherfordium. Some of the extraction systems under investigation use macrocyclic ligands, such as crown ethers. The high selectivity of these systems is used in a multitude of applications in analytical and technical chemistry. The coordination chemistry of macrocyclic ligands and alkali and earth alkali metals has been studied in depth [3], and these ligands are commonly applied for the separation of various metal ions [4].

The kinetics of the reaction is an important factor in developing suitable extraction systems for chemistry experiments with transactinide elements. The reaction should reach equilibrium as fast as possible. The size of the organic molecules used as ligands can have a large effect on the kinetics of the reaction.

The use of dicyclohexano-18-crown-6 (DC18C6) for the separation of zirconium and hafnium has been reported previously [5], but this study was not conducted on a time scale short enough to ensure that the reaction kinetics are fast enough to allow the study of rutherfordium. In this work, the extraction of zirconium and hafnium with DC18C6 from various concentrations of hydrochloric acid was studied using isotopes with minute half-lives. The distribution ratios for the elements were determined as a function of acid and ligand concentration.

The online experiments were performed at the 88-inch cyclotron at LBNL using the short-lived isotopes <sup>85</sup>Zr ( $T_{1/2} = 7.9$  m) and <sup>169</sup>Hf ( $T_{1/2} = 3.25$  m). Details on the production of the isotopes as well as the transport of the radionuclides to the chemistry setup are given in a second contribution to this annual report [6].

The produced and pre-separated isotopes were dissolved in 50  $\mu$ L HCl of appropriate concentration and transferred to

a centrifuge cone containing additional 3950  $\mu$ L of the same acid. The aqueous phase was mixed with an equal volume of crown ether diluted in dichloromethane. Phases were vigorously mixed for 20 seconds and centrifuged for 20 seconds. Afterwards a 3-mL aliquot was taken from each phase and assayed using a HPGe  $\gamma$ -ray detector.

Figure 1 shows the yield for the extraction of Zr and Hf with 0.025 M DC18C6 from 7.0 – 10.5 M HCl. Zr extraction starts above 7.0 M and increases sharply between 7.0 and 7.5 M. The Hf extraction increases significantly in the concentration range between 8.0 and 9.5 M. The extraction yield reaches a maximum of 91% for Zr and 88% for Hf.

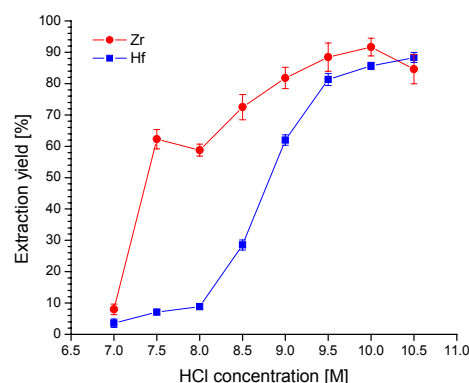


FIG. 1: Zr and Hf extraction from 8.0 – 10.5 M HCl into 0.025 M DC18C6 in  $\text{CHCl}_3$ .

The separation factor between Zr and Hf, defined as the ratio of extraction yields, reaches a maximum of  $\sim 9$  at a hydrochloric acid concentration of 7.5 M and decreases with increasing acid concentration.

Further studies are necessary to determine the influence of short mixing times on the extraction yield and the separation factor.

## REFERENCES

- [1] J.P. Omtvedt et al., J. Nucl. Radiochem. Sci. **3**, 121 (2002).
- [2] R. Sudowe et al., Ernest Orlando Lawrence Berkeley National Laboratory, LBNL-49957 (2002).
- [3] J. W. Steed, Coordin. Chem. Rev. **215**, 171 (2001)
- [4] A. T. Yordanov, D. M. Roundhill, Coordin. Chem. Rev. **170**, 93 (1998)
- [5] N. V. Deorkar, S. M. Khopkar, Anal. Chim. Acta **245**, 27 (1991)
- [6] R. Sudowe et al., contribution to this annual report